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Biogenic Hydrocarbon Contribution to the Ambient Air of Selected Areas - Tulsa; Great Smokey Mountains; Rio Blanco County, Colorado

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January 1980

BIOGENIC HYDROCARBON CONTRIBUTION TO THE AMBIENT AIR OF SELECTED AREAS

Tulsa
Great Smoky Mountains
Rio Blanco County, Colorado

by

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PREFACE

Scientists have hypothesized for a number of years that the atmospheric loading of nonmethane hydrocarbons from biogenic sources is as large or even larger than emissions from anthropogenic sources. Evidence cited to support this hypothesis includes the phenomenon of blue haze observed in the Smoky Mountains, high total nonmethane hydrocarbon concentrations measured in rural areas, and even detailed chromatographic analyses of air in rural areas that supposedly identify specific biogenic hydrocarbons. The sampling efforts described herein were undertaken to determine the credibility of these speculations. In particular these studies addressed the questions: Do biogenic hydrocarbons constitute a large portion of the total nonmethane hydrocarbon concentration in these areas? What portion of the total nonmethane hydrocarbons can be attributed to auto exhaust?

ABSTRACT

Estimates of volatile hydrocarbon emissions to the atmosphere indicate that biogenic sources are much greater on a global basis than anthropogenic sources. Many assumptions inherent in these estimates, however, introduce a large degree of uncertainty about both inventories.

A critical review of the literature reveals nonmethane hydrocarbons in rural and remote areas consist mainly of anthropogenic species, and are composed of less than 10% biogenically-related compounds (i.e., monoterpenes and isoprene). Despite these results, some investigators continue to invoke "natural hydrocarbon emissions" to explain naturally occurring haze, incorrectly identified gas chromatographic peaks, and high concentrations of total nonmethane hydrocarbons that are measured by indiscriminate (total hydrocarbon-methane) analyzers.

In response to the suggestion that biogenic emissions are responsible for the high hydrocarbon concentrations described in several reports, the Environmental Sciences Research Laboratory of the U.S. Environmental Protection Agency initiated short-term sampling as a means of validation. A limited number of whole-air samples were collected in Tedlar bags and analyzed by gas chromatography with flame ionization detection.

The areas of study included: Tulsa, Oklahoma; Rio Blanco County, Colorado; and the Great Smoky Mountains in Tennessee. Tulsa air was found to contain an average of 0.2% isoprene of the total nonmethane hydrocarbon load. Rio Blanco County and the Smoky Mountain air, respectively, averaged about 2% and 4% biogenic hydrocarbon of the total nonmethane hydrocarbon loads. Isoprene appears to be a dominant olefin in rural and remote areas.

Although the tests were of short duration, the results suggest monoterpenes and isoprene constitute minor components of rural air relative to anthropogenic hydrocarbons.

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SECTION 1

INTRODUCTION

In 1960 Went proposed that vegetation releases 165 x 10^6 ton/yr of volatile organic matter globally, in the form of terpenes (1). He speculated the hydrocarbons thus liberated could be responsible for the formation of atmospheric blue haze created as a result of terpene-ozone oxidation products (2). Hazes of this type are especially prevalent over areas such as the Smoky Mountains of Tennessee and the eucalypt forests of Australia.

Through the 1960's, Went's original estimates were revised upward by Rasmussen and Went (3) and by Ripperton et al. (4). All of the estimates were crude, as the authors pointed out, being based upon a number of tenuous assumptions. Nevertheless, in 1968 at the Stanford Research Institute, (5) in a literature review conducted for the American Petroleum Institute annual biogenic emissions were determined as exceeding anthropogenic emissions on a worldwide basis (120 x 10^6 tons vs 27 x 10^6 tons). Since the above report, further studies have attempted to refine these estimates and reduce some of the uncertainties inherent in them. The result has been to revise the biogenic estimates upward further, while only marginally improving the uncertainties.

Chief among the uncertainties is the generation of scaling factors used to extrapolate the emission of a branch or small forest plot to a large area of diverse and discontinuous vegetation. The short-comings in the accuracy of the emission inventories (biogenic and anthropogenic) are supported by actual measurements of ambient hydrocarbons in rural and remote areas. Although the data base is not large, published measurements of total nonmethane hydrocarbons (TNMHC) within forested areas have never shown more than a 40 to 50% contribution of biogenic hydrocarbons. Typically the contribution is less than 10%, even in densely forested areas. Measurements of detailed hydrocarbon concentrations where isoprene and monoterpenes

were specifically sought out are summarized in Table 1. Studies where only TNMHC was measured are excluded because (1) high TNMHC in rural or remote areas may be the result of urban influences and (2) the accuracy of the TNMHC method has been seriously questioned (6,7).

In examining the compounds and concentrations reported, consideration must be given to the type of vegetation in the sampling area and its density upwind of the sampling location; furthermore, concentrations are strongly influenced by the degree of atmospheric mixing, the season and temperature. Lastly, the techniques used in making the hydrocarbon measurements should be examined along with the experience of the investigators employing those techniques. Most groups have used gas chromatographic (GC) separation with flame ionization detection (FID); however, the column types employed have a wide range of resolution. The lowest resolution is generally obtained with the short (2-6 m) packed columns. High resolution is obtained with the support-coated open tubular (SCOT) or wall-coated open tubular (WCOT) columns. Thus the probability of interferences occuring with a packed column are much higher than with a SCOT or WCOT column.

Interestingly, when average concentrations of biogenic hydrocarbons are examined in Table 1, the highest are reported by those studies where packed columns were employed (Rasmussen and Went (3), Whitby and Coffey(10)). Indeed average concentrations from such studies are ten to one hundred times higher than groups using high resolution columns. Furthermore, Rasmussen's later studies and those of his coworkers at Washington State University employing high resolution GC never reported concentrations of those magnitudes, i.e. Rasmussen et al. (9) and Holdren et al. (15). The work of Whitby and Coffey (10) should be viewed with some caution since these experimenters did not match retention times on their packed column, but chose to group compounds as 'terpene species' when eluting after a particular time, or as 'lighter species' when eluting before this time. Because of the rural nature of the site, they discounted urban influences and believed their data reflected only natural sources.

If the work of Rasmussen and Went (3) and Whitby and Coffey (10) is discounted, the data reported in Table 1 agree reasonably well. Isoprene

Table 1. SUMMARY OF BIOGENIC HYDROCARBON CONCENTRATIONS IN AMBIENT AIR

Authors/Sampling location(s)	Reference number	Surrounding vegetation	Biogenic hydrocarbon	Avg. conc., ppbC	Max ppbC	Min ppbC	TNMHC ppbC	% biogenic	% automotive	Comments
Rasmussen & Went Ozark Plateau, Missouri	(3)	Hardwood forest & prairie	isoprene α-pinene p-pinene limonene myrcene	totaled 106	150	70	--	--	--	Lowest levels observed just before sunrise; high levels observed when deciduous foliage changes color in the autumn; high level of volatiles observed after grass was mowed; packed column gc-fid.
Gray Summit, Missouri		Junipers & meadow	totaled	41	60	30	--	--	--	
Highland Biological St., NC		Hardwood forest	totaled	50	120	10	--	--	--	
Gray Summit, Missouri		Hardwood forest & meadow	totaled	109	340	10	--	--	--	
Rasmussen, Chatfield et. al. Elkton, Missouri	(8)	Hardwoods & farmland	isoprene	6	28	0	98	6	12	79 measurements; most intensive study yet performed; gc-fid high resolution SCOT column.
Lonneman et. al. Chickatawbut Hill, Mass.	(9)	Oak & other hardwoods	isoprene	10	34 (1 day)	< 1				WCOT column; highest levels observed during daylight hours.
Whitby & Coffey Adirondack Mountains, NY	(10)	Coniferous forest	'terpene species'	33	72	5.3	--	--	--	Chromatographic peaks not identified; authors assumed biogenic origin due mainly to rural location; packed column gc-fid.
			'lighter species'	63	123	29.3	--	--	--	
		Deciduous/coniferous forest	'terpene species'	12	17	6.5	--	--	--	
			'lighter species'	18	21	14	--	--	--	
Lonneman, Seila, Bufalini St. Petersburg/Tampa, Miami and the Everglades, Florida	(11)	Orange groves, gum, cyprus, oak, wax myrtle, black willow, persimmon	isoprene d-limonene α-pinene β-pinene	1.6 0 0 0	4.5 -- -- --	< 0.1 -- -- --	106 --	4 (max)	61	gc-fid; WCOT columns.
Schjoldager & Wathue Gjerdrum, Norway	(12)	Coniferous forest (spruce & farmland)	α-pinene β-pinene limonene isoprene	14.0 9.5 -- --	16.5 19.5 trace --	10.5 3.0 -- < 0.5	--	--	--	High resolution glass capillary column used; 3 data points.
Seila Jones State Forest, (38 mi North of Houston, TX)	(14)	Loblolly pine	α-pinene isoprene	3.6 0.1	7.7 1.2	< 0.1 < 0.1	357	2	35	gc-fid; WCOT columns.
Holdren, Westberg & Zimmerman Moscow Mountain, North-Central Idaho	(15)	Coniferous forest (pine and fir)	α-pinene β-pinene 3-carene limonene	1.13 0.86 0.64 0.10	7.3 4.6 5.4 0.5	0.1 < 0.1 < 0.1 < 0.1	samples collected within the forest 3 ft above the ground.			Samples collected outside the forest contained no measurable terpenes (less than 0.1 ppbC); gc-ms with single ion peak monitoring.
			α-pinene β-pinene 3-carene limonene	1.23 1.73 1.08 0.10	2.7 5.7 3.7 0.2	0.3 < 0.1 < 0.1 < 0.1	samples collected within 1 inch of the forest floor leaf litter			

averages fall between 0.1 and 10 ppbC, except for extremes as high as 34 ppbC and less than 0.1 ppbC in areas where isoprene-emitting vegetation was present. Alpha-pinene, being the predominate monoterpene, averages between less than 0.1 ppbC to 14 ppbC, with maximums as high as 16.5 ppbC (reported in Norway).

The above summarized concentrations with the exceptions noted represent biogenic contributions to the TNMHC burden of less than 10% in their respective areas. Recently, however, the Environmental Sciences Research Laboratory has been requested to perform detailed hydrocarbon analyses of ambient air from several areas of the United States suspected of carrying a large fraction of biogenic hydrocarbons. This report details the results of those analyses. The samples were collected during July 1978 in Tulsa, Oklahoma, and around the Piceance Creek area of Rio Blanco, Colorado; samples were also collected and analyzed from the Great Smoky Mountains in Tennessee during the last week of September 19th.

SECTION 2

CONCLUSIONS

Three areas of the United States were studied to determine if the ambient air contained significant concentrations of hydrocarbons of a biogenic nature. None of these areas was found to contain a large fraction of biogenic nonmethane hydrocarbon. The Tulsa, Oklahoma air samples consisted of 30 to 55% auto exhaust in the city and 8 to 24% auto exhaust at a downwind rural location. Most of the balance of the TNMHC appears to be composed of paraffins, similar to the refinery/tank farm emissions. Biogenic hydrocarbons (isoprene) contributed an average of only 0.2% to the TNMHC (ranging from 0 to 0.5%). Of the eight samples collected in Tulsa, isoprene was detected in only four samples; the highest concentration observed was 1.2 ppbC.

The samples collected in Rio Blanco County, Colorado, and the Smoky Mountains, Tennessee, contained low TNMHC concentrations. Rio Blanco County samples ranged from 117 to 138 ppbC. Twenty to thirty percent could be attributed to auto exhaust; most of the balance of the TNMHC was within the paraffin range, suggesting distant urban sources or local natural gas activities. Isoprene, present in most samples in amounts ranging from 0.1 to 5.6 ppbC, contributed approximately 2% to the already low ambient TNMHC concentration.

The Smoky Mountain samples similarly contained low TNMHC concentrations, ranging from 87 to 171 ppbC. Although a large fraction of this total apparently can be attributed to auto exhaust, the acetylene tracer technique used to verify the origins of this chemical could not be employed accurately, since local wood-burning campfires were also likely to be significant sources of acetylene. Biogenic emissions nevertheless contributed an average of 4% to the TNMHC, and a maximum of 6% in the form of isoprene and alpha-pinene. Note: p-xylene and alpha-pinene have the same GC retention time, which

could create too high a biogenic estimate for this series of analyses.

Isoprene was the predominant olefin species in 50% of the Colorado samples and 33% of the Smoky Mountain samples. However, in both cases the concentration never exceeded 7 ppbC.

Although this study represents a relatively short-term effort, the results suggest that biogenic hydrocarbons (isoprene and the monoterpenes) constitute less than 10% of the TNMHC burden of rural air. These results are consistent with most previously-reported concentrations in forested rural areas.

SECTION 3

RECOMMENDATIONS

This study again serves to point out that urban centers influence ambient pollution levels in distant rural or remote areas. Investigators have often erroneously attributed high hydrocarbon levels in these areas to natural sources, simply because of the remote geography. However, in the case of the high TNMHC levels reported in Rio Blanco County, Colorado, transport from urban centers does not explain levels on the order of 8 ppmC, nor, as suggested by this study, do biogenic sources. Rather, the monitoring station reporting these high TNMHC levels was apparently sampling its own etylene effluent from the ozone monitor. It therefore cannot be overemphasized that such monitoring stations should take extreme care in checking plumbing for leaks and in installing properly functioning ethylene combustors on monitor exhaust. Alternatively, a monitor that does not use ethylene could be used for sampling, such as UV absorption instrumentation.

In future investigations, it is also recommended that analyses for ambient hydrocarbons larger than C_5 take advantage of the high resolution capabilities of capillary column GC. Application of this technology, by significantly reducing interferences, can improve confidence in identifying compounds by retention time. However, as pointed out by the initial Research Triangle Institute (RTI) misidentification of isoprene, measurements by retention time, even with a high resolution column, can still lead to incorrect identification. Additional confirmational techniques must be used where possible to provide supporting information, e.g., gas chromatography-mass spectrometry (GC-MS).

SECTION 4

EXPERIMENTAL

MATERIALS

Air samples were collected in 20-L Tedlar bags (Dupont 2 mil polyvinyl fluoride film). These were constructed by heat sealing a 1 m x 0.5 m sheet to form a 0.5 m square bag. Sample access was by way of a nut-secured O-seal straight thread adapter connected to a Swagelok quick connect. The bag was covered with 5 mil black polyethylene to protect the sample from sunlight. As Seila (13) has observed, Tedlar tends to contaminate air samples with acetone and acetaldehyde; the data reported for these compounds should be taken as upper limits.

The bags were evacuated and filled using a Teflon-lined Thomas diaphragm pump (Model 107CDC18TFE). The speed of the 12 V DC pumping motor was controlled by a variable rheostat (Ohmite, 100 W Model K, 10 Ohm). For the Smoky Mountain samples, a Metal Bellows pump (MB-41) was used for filling and evacuating the bags. Power for the Thomas pump was supplied by a 12 V auto battery; the metal bellows pump operated on 120 V AC.

Detailed hydrocarbon analyses were performed using the GC procedures described previously (14). Briefly, 3 column analysis of a cryogenically-concentrated air sample was performed to separate the C_2-C_{12} paraffins, olefins, and aromatics.

PROCEDURES

Before sampling, the bag was examined for leaks by checking for air pockets in the evacuated bags. The pump was started and the flow rate checked and adjusted as required. The 3 m, 0.64cm o.d. FEP tubing sampling inlet was placed upwind of the pumping system, then allowed to purge for a few minutes. Afterwards, the bag was connected and allowed to fill to

about 1/2 volume (10 L). The bag was filled to only 1/2 volume to allow for expansion when the bag was shipped by air freight for analysis.

SECTION 5

SAMPLING LOCATIONS

TULSA, OKLAHOMA

Of the four sampling sites chosen in the Tulsa area, three had been used earlier by RTI in a 1977 study (16). These were: the City-County Health Department, the Post Office, and Liberty Mounds (See Figure 1). These sites were chosen since RTI reported measuring very high concentrations of isoprene and ethylene during their earlier field study. The Post Office is located in the downtown section of Tulsa, while the City-County Health Department is within the city limits, but near the suburbs. The Liberty Mounds location is a rural area that is usually upwind of Tulsa, but was downwind during this study. The sampling site is about 37 km south of Tulsa. The fourth sampling location was a roadside approximately 0.8 mile downwind of the Texaco refinery complex in Tulsa; grab samples were collected there to obtain a rough characterization of refinery emissions.

RIO BLANCO COUNTY, COLORADO

The Piceance Creek basin of Rio Blanco County, Colorado, is located approximately 80 km northeast of Grand Junction, Colorado, and 24 km north of Rifle (see Figure 2). The terrain is rocky and arid, possessing only sparse vegetation: sage brush, coarse grass, pinyon pine and some juniper. Much of the land in this area is federally owned, of which a part is leased to oil companies for possible shale oil development (see Figure 3).

One area for potential development is a tract referred to as Cb, which is leased to Occidental Oil and Ashland Oil (O & A). In order to estimate the impact of oil shale development on air quality, O & A established an air monitoring station at Cb in 1974 to gather baseline data on the criteria pollutants. The station has since been recording

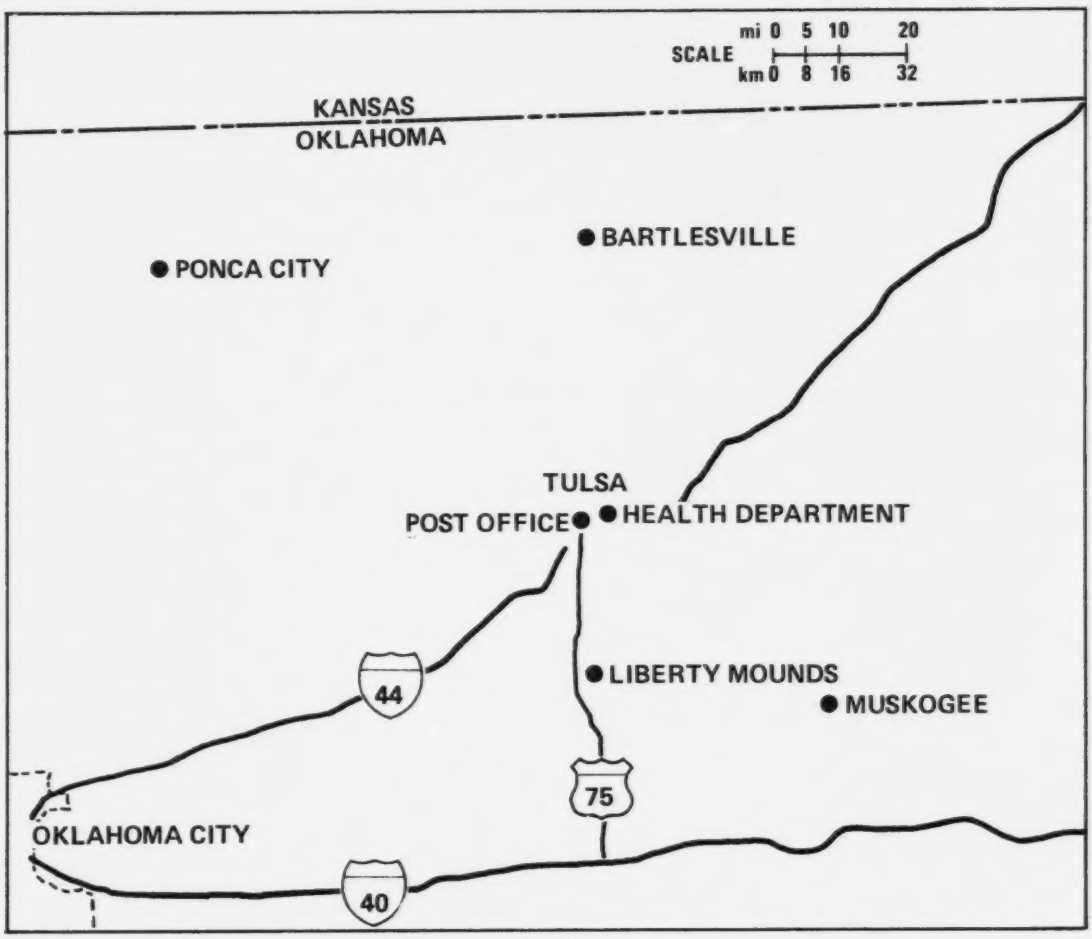

Figure 1. Tulsa, OK sampling locations.

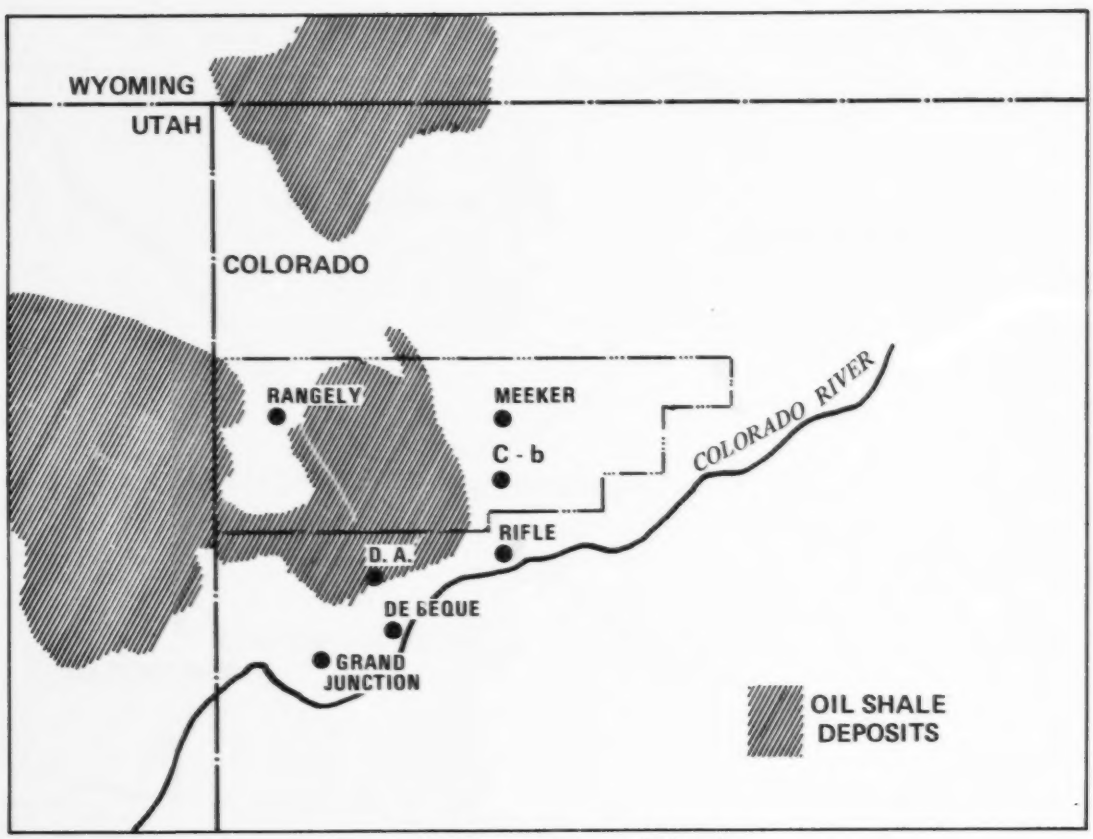

Figure 2. Rio Blanco county, Colorado.

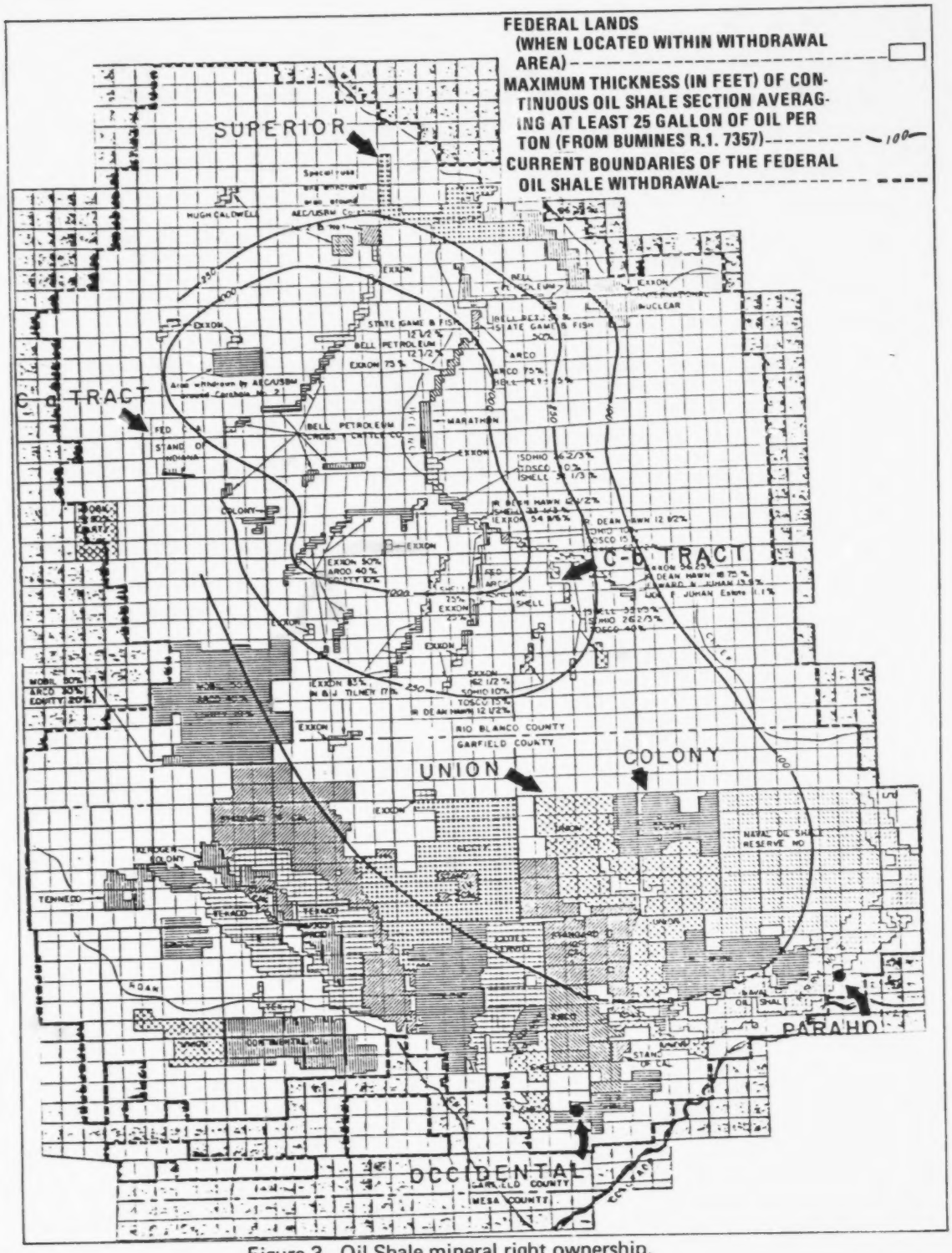

Figure 3. Oil Shale mineral right ownership.

periodic TNMHC excursions in concentrations as high as 4 to 7 ppmC, while the other pollutant concentrations are very low. Additional samples were collected upwind of the monitoring station approximately 4.5 km to the south, and at a site 4.3 km north in the valley (see Figure 4). Also, one sample was taken downwind of the Mobil Oil natural gas processing facility at Piceance Creek (about 9.6 km NNE of the monitoring station).

GREAT SMOKY MOUNTAINS NATIONAL PARK

Samples were collected in Sevier County, Tennessee in the Great Smoky Mountains National Park. The sampling site was at a National Park Service building at Elkmont about 10 km southwest of Gatlinburg, Tennessee. Elkmont Campground is nearby (see Figure 5). At an elevation of about 762 m, the surrounding 5 km is lushly forested with species that include: Canada hemlock, eastern hemlock, pitch pine, white ash, yellow buckeye, sugar maple, basswood, yellow birch, yellow-poplar, American beech, mountain silverbell, black cherry, mountain laurel, northern red oak, rhododendron, and cucumber tree.

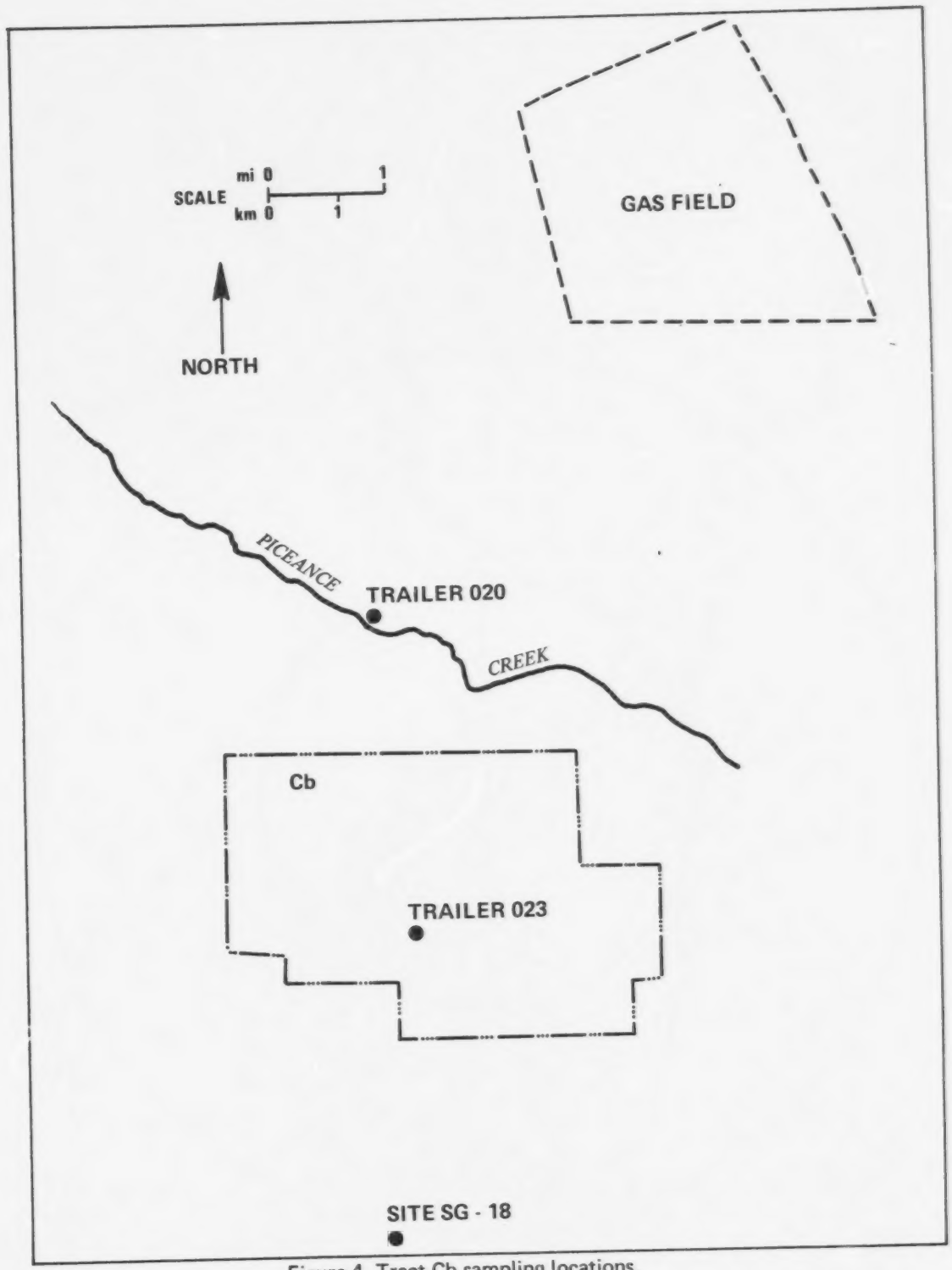

Figure 4. Tract Cb sampling locations.

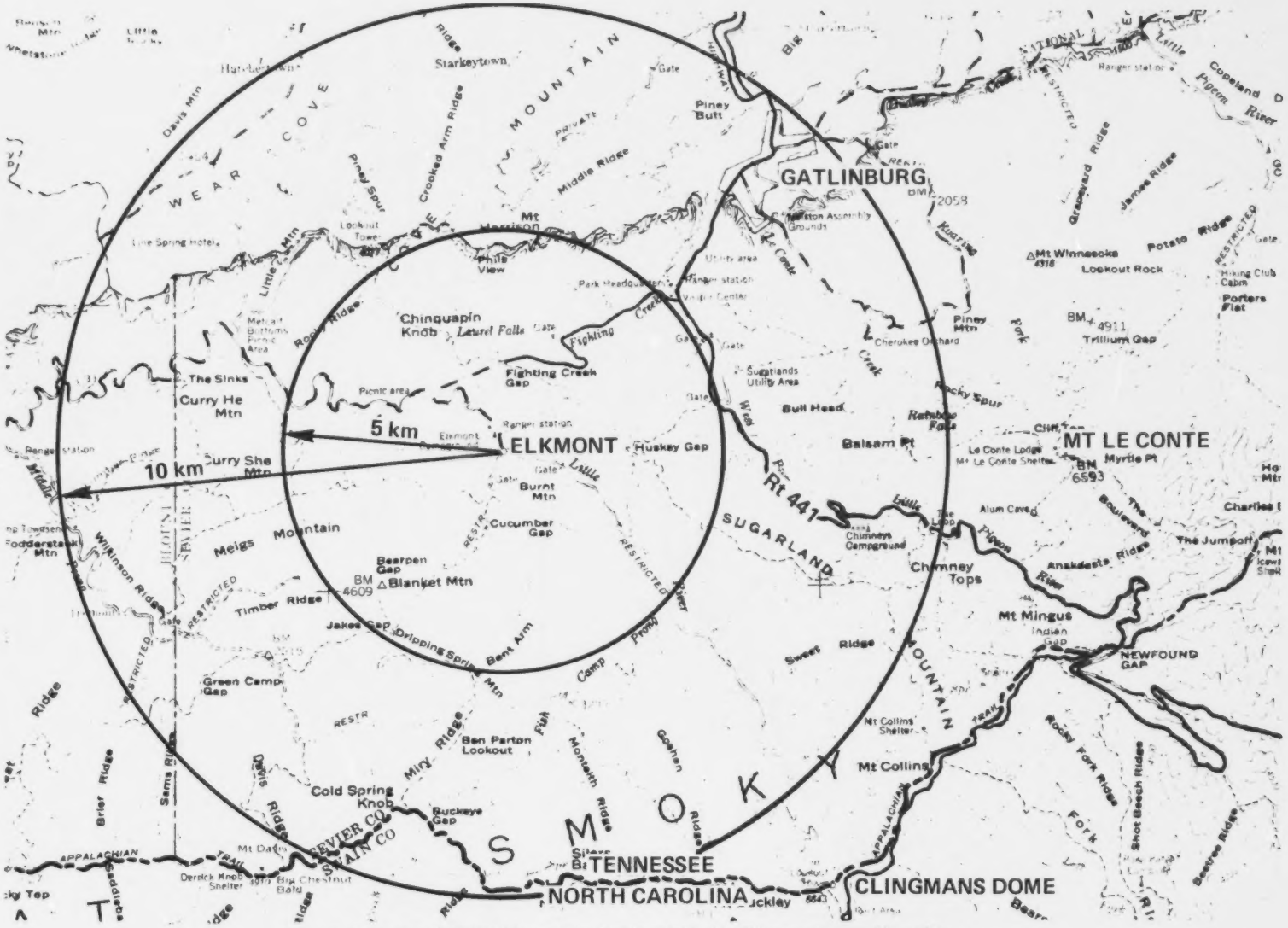

Figure 5. Great Smoky Mountain National Park: Elkmont sampling site.

SECTION 6

RESULTS AND DISCUSSION

TULSA, OKLAHOMA

On July 27, 30-min integrated air samples were collected at three sites in and around Tulsa, Oklahoma. Two consecutive samples were collected at the City-County Health Department, two at the downtown Post Office and two at the rural Liberty Mounds site approximately 37 km south of Tulsa. The winds were out of the north, in contrast to more typical southerly winds in the area. The Liberty Mounds site, used as an upwind station in the RTI study, therefore represents the downwind plume of Tulsa in these samples. In addition to the three sites, which had been used by RTI, two grab samples were collected downwind of the Texaco Refinery in Tulsa to obtain a hydrocarbon fingerprint of refinery emissions.

Table 2 presents detailed hydrocarbon profiles of the samples collected. Of particular interest are the low values of isoprene observed; in contrast to preliminary average values of 74 to 118 ppbC observed by RTI, the highest concentration observed in this study was only 1.2 ppbC. Also, only 1 ppbC of ethylene was observed at the rural Liberty Mounds site, whereas RTI reported a preliminary average of 2028 ppbC.

Table 3 presents summations of the paraffins, olefins, and aromatics, and their ratios to acetylene. By normalizing to acetylene, as described by Lonneman (18), the contribution of tailpipe emissions to the NMHC can be estimated. As is apparent most of the aromatics and olefins can be attributed to tailpipe emissions in the Health Department and Post Office samples. However, the paraffins appear to have other sources, such as natural gas emissions, gasoline evaporative emissions, or possibly the refinery operations (as indicated by their heavy emissions in the paraffinic range). The consecutive samples collected at Liberty Mounds seem to indicate transport

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Table 2. HYDROCARBON COMPOSITION OF TULSA AREA AIR

Location:	City County Health Department		Post Office		Liberty Mounds		Texaco Refinery	
Date:	7-27-78		7-27-78		7-27-78		7-27-78	
Wind:	From N to NNE, light		"		From N to NE, light		From N to NE, light	
	Time							
Compound	8:25-8:55 AM	8:55-9:25 AM	9:53-10:23 AM	10:33-11:03 AM	11:51-12:25 PM	12:25-12:55 PM	1:30-1:33 PM	1:33-1:35 PM
Paraffins								
ethane	11.7	10.2	10.7	7.2	4.1	2.3	33.8	73.5
propane	15.5	14.2	9.6	8.9	4.6	8.2	95.5	189.8
isobutane	8.1	8.3	14.1	12.9	10.8	30.1	86.9	236.7
n-butane	16.5	19.1	51.7	48.7	40.5	121.8	175.2	342.7
isopentane	17.3	20.1	65.8	65.9	52.8	153.5	53.8	113.1
n-pentane	12.2	18.4	40.8	40.9	30.1	86.1	46.4	81.7
cyclopentane	2.5	3.2	5.8	4.6	5.3	8.5	5.2	6.4
2-methylpentane	6.4	8.0	23.9	19.6	13.2	35.4	15.8	39.8
3-methylpentane	4.6	5.6	13.8	13.0	8.0	17.6	4.9	21.7
n-hexane	6.1	6.2	14.6	14.0	8.7	19.3	12.3	32.4
2,4-dimethylpentane	5.2	5.5	17.8	14.7	8.4	19.2	19.5	36.5
methylcyclopentane	0	0	0	0	0	0	0	0
cyclohexane	1.8	3.3	0	1.4	2.7	2.7	9.0	14.8
2-methylhexane	5.0	4.9	17.1	7.5	3.5	4.8	4.8	10.3
2,3-dimethylpentane	3.3	3.3	7.4	4.2	2.6	4.2	2.5	9.0
3-methylhexane	5.7	5.4	15.0	7.8	3.0	5.8	6.5	15.4
cis-1,3-dimethyl-cyclopentane	1.0	0.7	4.3	1.6	1.3	2.5	3.1	7.7
2,2,4-trimethyl-pentane	4.6	4.1	8.5	5.7	2.1	4.3	6.3	17.1
trans-1,3-dimethyl-cyclopentane	2.0	1.2	3.7	0.7	0.7	1.7	4.6	10.3
n-heptane	6.1	4.9	10.5	5.8	6.1	5.3	9.0	21.4
methylcyclohexane	8.7	4.5	13.1	4.1	3.0	5.4	16.0	36.5
nonane	1.9	1.4	3.7	1.3	0.5	0.5	2.9	5.1
decane	2.3	2.0	3.5	1.8	0.6	0.7	4.0	6.9
undecane	2.2	0.8	1.9	0.4	0.3	0.5	0.5	2.9
Σ paraffins	150.6	155.2	357.4	292.6	212.7	540.3	618.3	1331.7
Olefins								
ethylene	11.5	8.6	6.5	7.3	1.0	1.0	5.9	20.4
propylene	4.2	5.6	3.2	2.8	1.9	--	27.5	109.9
isobutylene	1.2	1.5	4.6	4.3	3.7	11.9	15.7	60.2
trans-2-butene	1.6	1.6	4.5	4.7	3.7	9.4	7.5	28.8
cis-2-butene/butadiene	0	0	0	0	0	8.7	5.9	24.4
1-pentene	0.8	0.8	2.2	2.2	1.4	4.0	1.8	2.8
2-methyl-1-butene	0.6	1.1	3.4	3.1	2.3	6.4	2.4	3.5
trans-2-pentene	0	0	17.0	7.3	6.7	10.6	4.8	3.9
cis-2-pentene	0	0	7.5	5.6	5.3	7.3	4.6	3.0
2-methyl-2-butene	0	0	7.2	6.0	5.4	11.5	3.7	7.6
isoprene	1.2	1.0	0	0.3	0.3	0	0	0
4-methyl-2-pentene	0	0	1.0	0.8	0.4	1.1	0	0
1-hexene	0	0.5	0.7	0	0	0	0	0
trans-2-hexene	0.4	0.3	1.3	1.3	1.0	1.6	0.4	2.2
cis-2-hexene	0	0	0	0	0	0	0	0
Σ olefins	21.6	21.0	59.0	45.8	33.0	73.5	80.2	266.6
Aromatics								
toluene	13.8	13.0	15.2	14.8	5.9	7.3	14.3	25.5
ethylbenzene	2.6	2.6	3.1	2.5	0.9	1.2	4.6	7.9
p-xylene	1.6	2.4	2.4	2.0	0.7	1.0	2.8	4.9
m-xylene	5.3	5.2	5.4	5.4	2.3	2.8	9.9	11.1
o-xylene	3.3	3.2	3.8	2.5	1.1	1.7	5.8	9.3
isopropylbenzene	0	0	0	0	0	0	0	0
n-propylbenzene	0	0.9	0.8	0.9	0.6	0.6	0.7	0.7
m+p-ethyltoluene	0	0	0	0	0	0	0	0
1,3,5-trimethylbenzene	1.9	1.4	1.9	1.0	0.5	0.8	0.8	0.8
o-ethyltoluene	0	0	0	0	0	0	0	0
1,2,4-trimethylbenzene	7.1	3.7	6.2	1.3	0.9	2.0	3.6	3.6
m-ethyltoluene	3.3	0.5	1.3	1.3	0	0.1	0.5	0.5
Σ aromatics	39.0	32.8	40.1	31.7	12.8	17.7	43.1	64.2
Oxygenates								
acetaldehyde	7.0	8.3	--	--	--	--	--	--
acetone	18.1	14.6	52.8	4.8	19.8	5.6	6.9	10.1
Σ oxygenates	25.1	22.9	52.8	4.8	19.8	5.6	6.9	10.1
Σ Unknown-gc peaks (N)	42.3(16)	13.0(5)	50.4(15)	12.9(5)	10.7(8)	9.4(9)	15.8(8)	54.6(11)
acetylene	8.4	8.4	11.0	7.1	4.1	3.0	3.1	7.7
Total NMHC	287.0	253.4	568.1	394.9	293.1	649.5	767.3	1734.9

Table 3. SUMMARY AND ANALYSIS OF TULSA HYDROCARBON DATA

	City-County Health Department	City-County Health Department	Post Office	Post Office	Liberty Mounds	Liberty Mounds	Texaco Refinery	Texaco Refinery
	8:25 AM	8:55 AM	8:53 AM	10:33 AM	11:51 AM	12:25 PM	1:30 PM	1:33 PM
ΣP^*	150.6	155.2	357.4	292.6	212.7	540.3	618.3	1331.7
$\Sigma O^\dagger$	21.6	21.0	59.0	45.8	33.0	73.5	80.2	266.6
$\Sigma A^\ddagger$	39.0	32.8	40.1	31.7	12.8	17.7	43.1	64.2
$\Sigma P/C_2H_2$	17.9	18.4	32.4	41.0	52.1	180.1	199.5	172.5
$\Sigma O/C_2H_2$	2.6	7.5	5.3	6.4	8.1	24.5	25.9	34.5
$\Sigma A/C_2H2$	4.6	3.9	3.6	4.4	3.1	5.9	13.9	8.3
$\Sigma NMHC/C_2H_2$	34	30	51	55	72	216	248	225
%P from vehicular emissions	38	37	21	17	13	4	3	4
%O from vehicular emissions	127	130	61	50	40	13	13	9
%A from vehicular emissions	84	99	107	87	123	66	28	47
% vehicular	50	56	33	31	24	8	7	8
% biogenic (isoprene)	0.5	0.4	0	0	0.1	0	0	0

*P = paraffins

†O = olefins

‡A = aromatics

of hydrocarbons from Tulsa. The drop in contributions to the TNMHC burden from vehicular sources between the two sampling vicinities implies an increasing influence from other source(s), such as paraffins from the refineries. No monoterpenes were detected in any of the samples and only trace amounts of isoprene were found in four of the eight samples.

Since this study was performed, RTI has determined that the high ethylene concentration observed at Liberty Mounds was due to sampling echaust from their chemiluminescence ozone monitor (17). In addition, isoprene and trans-2-pentene has been determined as having nearly identical retention times on their GC column. Also, the large peaks identified as isoprene were found to be due to column substrate deterioration. Consequently, RTI has revised this downwind concentration to an average concentration of 1.6 ppbC (isoprene + trans-2-pentene).

RIO BLANCO COUNTY, COLORADO

In 1974, Occidental Oil and Ashland Oil established an air monitoring station in the remote Piceance Creek Basin of Rio Blanco County, Colorado. The station was instrumented to gather baseline data on the criteria pollutants on a tract of federal land leased to the oil companies. In so doing, the impact of future oil shale development operations on air quality can be assessed. As of November 1977, however, only some surface excavation and three access shafts have been started; the oil shale deposit has not yet been reached by the access shafts.

Some activity is occurring at the other sites surrounding Cb, but no large-scale operations have yet begun. Producing gas fields do exist nearby, however.

The air quality data collected thus far are typical of remote background concentrations of the criteria pollutants, with the exception of TNMHC. Concentrations in the range of 4 to 7 ppmC have been observed. These values seem inordinately high, not only for a remote area such as Cb, but even for a poorly ventilated city such as Los Angeles. The monitoring station in question has been audited by the U.S. Environmental Protection Agency (EPA), Environmental Monitoring and Support Laboratory (EMSL) and has met per-

formance specifications. Thus the frequent excursion of the TNMHC into the ppmC range has remained a mystery. Occidental Oil has suggested that the high levels may be caused by sage brush emissions, which are evidenced by a characteristic camphor aroma. Others have suggested that the oil shale deposit itself may be releasing volatile hydrocarbons.

In an attempt to provide some answers to these questions, air samples were collected at the Cb tract for detailed hydrocarbon analysis. Samples were collected in Tedlar bags on July 24 and 25, 1978 and shipped via air express to Research Triangle Park, North Carolina for detailed analysis. Samples were analyzed within 6 to 7 days after collection.

A total of six samples were collected at four sites. The sites are identified in Figure 4.

Trailer 023 on tract Cb is the air monitoring station which has been recording high hydrocarbon concentrations. At an elevation of 2115 m, it is situated on a ridge about 1.6 km south of the oil shale surface excavation activities. One sample was collected there at 12:50 pm on July 24 (see table 4), and one sample at 10:05 am on July 25 (see Table 5).

Site SG-18 is approximately 4.5 km to the south of trailer 023 on the same ridge but at a slightly higher elevation, 2249 m. Occidental Oil has anticipated that this will be the future site of the air monitoring station now at trailer 023. One sample was collected on July 24 at Site SG-18. Since surface winds were out of the south on July 24, this sample was representative of the air passing over Cb.

Trailer 020 lies in a valley about 4.3 km north of trailer 023. Though a monitoring station exists at Site 020, TNMHC was not measured. Two samples were collected at Site 020; one was taken at 3:27 pm on July 24 and one at 9:03 am on July 25. The last sample collected on July 24 was taken downwind of the Mobile Oil natural gas processing facility at Piceance Creek. Although during the sampling period this site was downwind of Cb, it was hoped that the hydrocarbon distribution from this facility would serve as a possible identifying fingerprint to natural gas emissions in the area. The Mobil gas field lies about 10 km NNE of Site 023.

Table 4. HYDROCARBON COMPOSITION OF RIO BLANCO COUNTY, COLORADO AIR

Location:	Trailer 023	Site SG-18	Trailer 020	Mobil Natural Gas Facility	Trailer 020	Trailer 023
Date:	7-24-78	7-24-78	7-24-78	7-24-78	7-25-78	7-25-78
Wind:	Var. S to N	S	E (up valley)	S (downwind)	E to NE	S
	Time					
Compound	12:50-12:55 PM	1:43-1:50 PM	3:27-3:31 PM	4:01-4:11 PM	9:03-9:08 AM	10:05-10:10 AM
Paraffins						
ethane	5.8	5.4	4.6	136.1	5.1	4.9
propane	3.2	3.9	6.3	465.3	5.7	5.3
isobutane	0.5	1.6	0.6	3.4	1.3	1.1
n-butane	1.4	1.0	1.5	56.0	0.7	1.4
isopentane	2.3	1.5	2.1	79.3	2.0	2.2
n-pentane	2.0	1.6	9.7	68.2	1.3	2.6
cyclopentane	1.5	1.0	0.5	9.3	1.3	0.5
2-methylpentane	2.3	2.5	1.3	49.5	0.8	1.3
3-methylpentane	3.7	1.6	0.9	27.1	0.7	1.4
n-hexane	3.2	1.7	1.1	58.8	1.0	1.0
2,4-dimethylpentane	3.9	4.1	0	37.4	1.6	1.9
methylcyclopentane	0	0	2.4	0	0	0
cyclohexane	0.6	0.6	0.1	31.9	0.2	0.4
2-methylhexane	4.1	2.3	1.7	23.4	0.7	1.7
2,3-dimethylpentane	1.7	0.7	0.6	8.0	0.2	1.7
3-methylhexane	5.5	2.3	2.1	27.3	1.3	1.6
cis-1,3-dimethylcyclopentane	0	0	0	11.2	0	0
2,2,4-trimethylpentane	0	0	9.3	16.6	5.3	0
trans-1,3-dimethylcyclopentane	13.1	6.6	1.4	0	1.4	7.5
n-heptane	3.5	1.4	0.6	50.7	1.4	1.4
methylcyclohexane	0	0.5	2.0	87.0	1.9	1.4
nonane	1.7	0.7	0.3	8.8	1.4	0.2
decane	3.6	1.7	1.3	5.4	1.7	1.6
undecane	2.3	1.2	0.8	1.6	1.1	2.5
Σ paraffins	65.9	43.6	51.0	1261.0	37.9	42.3
Olefins						
ethylene	25.5	1.3	1.2	2.6	1.3	1.4
propylene	2.8	1.2	1.0	1.0	0.5	0.9
isobutylene	0	0	0	5.4	0	0
trans-2-butene	0	0	0	1.6	0	0
cis-2-butene /butadiene	0	0	0	3.5	0	0
1-pentene	0.3	0.2	0	0.6	0	0.2
2-methyl-1-butene	0.7	1.2	0.7	10.7	0.7	0.4
trans-2-pentene	0	0	0	--	0	0
cis-2-pentene	1.7	0	0	--	0	0
2-methyl-2-butene	1.8	1.7	2.4	--	3.0	0.9
isoprene	0.1	1.8	5.6	0	3.9	0.9
4-methyl-2-pentene	0.2	0	0.2	0	--	--
1-hexene	0.3	0.5	1.1	0	0	0.1
trans-2-hexane	0.2	0	0.2	0	0	0
cis-2-hexene	0	0	0	0	0	0
Σ olefins	33.5	7.8	12.3	25.4	9.4	4.7
Aromatics						
toluene	10.9	7.4	5.0	17.5	5.3	4.8
ethylbenzene	2.2	1.1	1.0	3.6	0.8	0.9
p-xylene	2.0	1.2	0.8	1.8	0.9	2.0
m-xylene	4.2	2.0	1.3	5.1	1.6	0
o-xylene	3.6	3.2	2.2	3.6	3.3	2.9
isopropylbenzene	0	1.7	0	0	0	0
n-propylbenzene	1.6	0.8	0.5	0.8	0.8	0.7
m+p-ethyltoluene	0	0	0	0	0	0
1,3,5-trimethylbenzene	3.0	2.0	0.9	1.6	1.4	1.3
o-ethyltoluene	0	0	0	0	0	0
1,2,4-trimethylbenzene	10.9	6.0	3.2	3.8	6.5	4.4
m-ethyltoluene	3.8	0.4	0.3	4.8	5.3	5.3
Σ aromatics	42.2	25.8	15.3	42.7	25.8	22.4
Oxygenates						
acetaldehyde	9.4	7.8	6.2	--	5.2	5.4
acetone	23.7	18.0	16.7	16.9	5.1	11.8
Σ oxygenates	33.1	25.8	22.9	16.9	10.4	17.1
Σ Unknown gc peaks (N)	77.9(24)	24.1(12)	13.6(14)	158.6(34)	35.5(22)	49.3(22)
Acetylene	3.1	2.7	1.9	3.2	1.4	2.4
Total NMHC	255.7	129.8	117.0	1508.8	120.3	138.1

Table 5. SUMMARY AND ANALYSIS OF RIO BLANCO, COLORADO HYDROCARBON DATA

Site:	023	18	020	Mobil Gas	020	023	Tunnel samples (17)
Date: Time:	July 24 12:50 AM	July 24 1:43 PM	July 24 3:27 PM	July 24 4:01 PM	July 25 9:03 AM	July 25 10:05 AM	
ΣP	66.1	43.6	51.0	1262.0	37.9	42.3	--
ΣO	33.3	7.8	12.3	25.4	9.4	4.7	--
ΣA	42.2	25.8	15.3	42.7	25.8	22.4	--
$\Sigma P/C_2H_2$	21.2	16.5	26.4	389.5	27.7	17.6	6.8
$\Sigma O/C_2H_2$	10.7	2.9	6.4	7.9	2.9	1.5	3.2
$\Sigma A/C_2H_2$	13.5	9.7	7.9	13.2	8.0	6.9	3.9
$\Sigma NMHC/C_2H_2$	82.0	49.0	60.6	465.7	87.8	57.3	17
% vehicular emissions	21	35	28	4	20	30	100
% biogenic (isoprene)	0	1	5	0	3	1	--

In general, the absolute levels of TNMHC were low. With the exception of the sample from Site 023 on July 24, the samples ranged from 117 to 118 ppbC at Site SG-18, trailer 023 and trailer 020. Apparently, the lone sample above this range was contaminated by the evaporative emissions/exhaust from the vehicles parked in close proximity, and by ethylene exhaust from the ozone monitor. As was noted at the time of sample collection the wind shifted when this was being collected resulting in the collection of air that had passed over the monitoring trailer. This was not a problem in subsequent samples.

In order to estimate what portion of the TNMHC was due to vehicular emissions alone, the technique of Lonneman et al. (18) was again employed. This method uses acetylene as a normalizing compound to estimate the contribution of auto exhaust to the hydrocarbon burden. An implicit assumption is that acetylene is emitted in significant concentrations only by the combustion process of autos, and that under normal operating conditions automobiles will also emit a number of paraffins, olefins, and aromatics in proportion to acetylene. The limitations of this method are described by Lonneman et al. (18).

Normalization of TNMHC and the individual groups (paraffins, olefins, aromatics) to acetylene is shown in Table 5. As is evident, only 20 to 35% of the hydrocarbons are directly attributable to tailpipe emissions. But as Lonneman demonstrated, in industrialized areas, the contribution of auto exhaust may be very high during morning rush hour traffic yet at later times and under different meteorological conditions, other significant hydrocarbon sources may exist: industrial emissions, carburetor evaporative emissions, and gasoline spillage. Consequently, in a remote area such as Cb, an urban plume would appear as a photochemically-exhausted, well-mixed air mass containing mostly lesser reactive paraffins and some aromatics. The exact distribution would depend on the emission characteristicis of the urban area as well as the transport time period of the urban plume.

Biogenic hydrocarbons do not seem to be present in significant concentrations at Cb. Isoprene was not seen at more than 5.6 ppbC; nonetheless, this compound was the most prominant olefin in half of the samples (exclusive

of the Mobil gas facility). The monoterpenes that are known to be emitted by sage brush (19) were not seen. (It should be noted, however, that the major sage volatile, camphor, has not been run through ESRL sampling and analytical procedures to determine if our GC system would see this component-camphor is a high boiling oxygenate.) The other identified sage volatiles will be determined by our system if present, including: 1,8-cineol, alpha-pinene, beta-pinene, camphene, limonene, cymene, myrcene, beta-phellendrene, and γ-terpinene. Also of note is that if the reported high hydrocarbon concentrations are due to the terpenic emissions of sage, then an inverse relationship should be seen between ozone and TNMHC in an NO_x-defficient atmosphere. At ppm concentrations, the highly reactive terpenes will react with ambient ozone very quickly. Such observations were not observed (LaHue, personal communication). The C_2-C_5 paraffins, however, could coexist with ozone since their reaction is very slow.

A closer examination of the hydrocarbon distribution reveals that paraffin to C_2H_2 ratio is particularly high; this seems to be caused by relatively high concentrations of the C_2 to C_5 paraffins. Either the makeup of the incoming air mass (as noted previously) or local natural gas emissions could be the source of the high concentrations. Though the downwind sample of the Mobil Piceance Creek Gas Field shows elevated levels of the C_2 to C_5 paraffins, it is not possible to determine from this small sampling effort which of these sources may be more significant. The total hydrocarbon analyzer was not operating in the methane mode during our visit. It read only 2.0 ppmC total hydrocarbon (THC) on July 24, and 1.6 ppmC THC on July 25. These readings are not grossly inconsistent with the detailed analyses presented here, assuming a background of methane of about 1.5 to 1.6 ppm.

Since the high TNMHC reported at Cb do not seem to correlate with meteorological parameters of season (Lahue, personal communication), or display an inverse relationship to ozone, biogenic emissions and transport from distant urban areas seem unlikely explanations of this phenomenon. The hydrocarbon distribution suggests a greater than usual presence of lighter paraffins due possibly to the local emissions of gas fields. However, if such were the case, then some correlation should be observed with wind direction or mixing heights.

It is the opinion of these investigators that the previously reported high values are possibly due to a malfunctioning hydrocarbon analyzer, or more likely, to sampling of ethylene used for the ozone monitor. Ethylene contamination is frequently encountered around such monitors. Monitors must be equipped with catalytic combustors to destroy ethylene in the exhaust, and the ethylene feed system plumbing must be thoroughly checked for leaks (i.e., regulator fittings, diaphragms, fittings in the instrument). Ethylene contamination from the monitoring station was suggested in the July 24 trailer 023 sample since shifting winds caused station backwash to be sampled.

GREAT SMOKY MOUNTAINS NATIONAL PARK, TENNESSEE

When the issue of natural organic emissions was first discussed by Went (2), the blue haze that gives the Smoky Mountains their name was proposed to be caused by the oxidation of terpenes to aerosols. However, no attempts to measure ambient terpene concentrations in the Smokies have been reported. Hence, a 2-day sampling effort was undertaken to determine the hydrocarbon composition of Smoky Mountain air.

The results of the analyses are shown in Table 6. To determine the auto exhaust contribution, the data have been normalized to acetylene as described previously (Table 7). This procedure yields vehicular contributions to the samples ranging from 38 to 119%. It is likely that some of these samples were influenced by acetylene source(s) other than auto exhaust, since the procedure as a sole tracer for this source yields contributions greater than 100%. Campfires at a nearby campground were also probable sources of the compound, since acetylene has been identified as a major component of the incomplete combustion of wood and plant matter (20).

The concentrations of TNMHC averaged quite low. With the exception of two of nine samples, which were probably influenced by early morning vehicular traffic and smoldering campfires, the concentrations ranged from 87 to 114 ppbC. Isoprene was the dominant olefin in three of the nine samples, but was not higher than 6 ppbC. The combined contribution of the biogenic hydrocarbons isoprene and alpha-pinene to the TNMHC in all samples was at least 1%, but no higher than 6%. Of note is that alpha-pinene and

Table 6. HYDROCARBON COMPOSITION OF SMOKY MOUNTAIN AIR

Date	9-25-78	9-25-78	9-25-78	9-25-78	9-25-78	9-26-78	9-26-78	9-26-78	9-26-78
	Time								
Compound	6:00-8:00 AM	10:00-10:20 AM	12:00-12:15 PM	2:15-2:45 PM	4:00-4:20 PM	8:25-8:27 AM	8:30-8:34 AM	10:00-10:20 AM	11:30-11:35 AM
Paraffins									
ethane	10.2	9.4	11.7	16.0	11.3	15.9	10.7	8.8	8.6
propane	9.2	5.8	7.9	8.4	7.3	13.3	11.3	5.4	5.0
isobutane	2.7	2.3	2.0	2.2	1.7	5.5	2.5	1.9	2.1
n-butane	3.8	5.1	4.0	4.6	3.6	7.6	5.5	4.4	4.6
isopentane	4.5	5.6	3.2	3.7	3.0	6.9	6.4	5.2	5.3
n-pentane	3.3	4.0	1.9	2.6	0.4	4.1	4.0	2.8	3.3
cyclopentane	0.7	1.1	0.4	0.4	0.9	1.7	1.6	0.9	0.7
2-methylpentane	1.5	2.7	1.0	1.1	0.8	4.3	4.1	2.4	2.2
3-methylpentane	1.0	1.4	0.7	0.7	0.7	3.1	2.4	1.1	1.0
n-hexane	1.0	1.8	0.7	0.8	0	2.4	2.6	1.2	1.5
2,4-dimethylpentane	0	0	0	0	0.6	0	0	0	0
methylcyclopentane	1.2	1.5	1.2	0	0.5	2.1	1.6	1.1	0
cyclohexane	1.0	0.8	0.1	0	0	1.2	1.2	0	0
2-methylhexane	3.2	1.8	0.2	0	0	1.3	2.4	1.4	0
2,3-dimethylpentane	1.3	1.0	0.1	0.5	0	0.9	1.1	0.7	0.5
3-methylhexane	0.6	1.0	0.2	0.1	0.3	1.6	2.0	1.2	1.3
cis-1,3-dimethylcyclopentane	1.0	0.4	0	0.4	0	0.9	0.3	0	0.8
2,2,4-trimethylpentane	0	0.9	0	0.8	0	0.7	0.8	0.8	0.6
trans-1,3-dimethylcyclopentane	0	0.2	0	0.4	0	0	0.3	0	0
n-heptane	0.5	0.8	0	0.7	0.3	0.4	1.1	0.6	0.9
methylcyclohexane	0	0.9	0	0	0.9	0.6	1.0	0	0.5
nonane	0.5	0.6	0.2	0.8	1.7	0.5	0.6	0.6	0.6
decane	0.4	0.3	0.6	0.6	0.9	0.4	0.8	0.9	0.4
Σ paraffins	47.4	49.3	36.1	44.8	35.0	75.5	64.1	41.5	39.8
Olefins									
ethylene	2.0	5.6	1.4	3.2	1.4	7.4	4.7	5.6	7.2
propylene	0.4	1.7	0.9	1.0	0.5	8.0	2.5	1.7	3.3
isobutylene	..	..	..	..	..	..	..	..	..
trans-2-butene	0.7	0.5	0.8	0.8	0.7	1.5	0.7	0.8	0.9
cis-2-butene/butadiene	0	0	0	0.4	0	0	0.5	0.6	0
1-pentene	1.1	0.3	0	0.3	0	0.5	0.4	0.3	0
2-methyl-1-butene	1.1	0.5	0.1	0	0	0.4	0.4	0.3	0
trans-2-pentene	0.3	0	0	0	0	0.8	0.8	0.5	0
cis-2-pentene	0	0	0	0.3	0	0	3.8	0	0
2-methyl-2-butene	0	0	0	0.4	0.1	0	3.7	0	0
isoprene	..	4.2	3.5	5.7	4.9	4.4	0.7	3.6	0
4-methyl-2-pentene	0	..	..	..	..	..	..	..	..
1-hexene	0	0	0	0	0	0.5	0.3	0	0
trans-2-hexene	0	0	0	0	0	0.3	0.3	0	0
cis-2-hexene	0	0	0	0	0	0	0	0	0
Σ olefins	5.6	12.8	6.7	12.0	7.6	23.7	18.8	13.3	11.2
Aromatics									
benzene	3.6	5.5	7.9	3.6	6.8	7.6	7.0	0.6	5.7
toluene	2.4	5.1	3.5	3.6	16.6	7.9	7.8	6.9	6.7
ethylbenzene	0.9	1.0	0.5	0.6	1.1	1.5	0.9	1.0	1.2
p-xylene/α-pinene	2.4	1.2	0.8	0.9	1.4	2.5	2.2	1.6	1.2
m-xylene	0.7	2.0	0.9	0.8	3.0	2.6	2.3	2.1	2.1
o-xylene	0.3	1.1	0.5	0.7	1.3	1.4	1.3	1.2	1.1
isopropylbenzene	0.7	0	0.3	0	0	0.6	0.3	0	0
n-propylbenzene	0	0	0	0	0.4	0.6	0.4	0	0
m+p-ethyltoluene	0	1.1	0	0	1.1	1.4	1.3	1.0	1.0
1,3,5-trimethylbenzene	0	0.5	..	0	0.5	0	0.8	0.7	0.4
o-ethyltoluene	0	0.7	0.6	0.6	1.0	0	0	0.6	0.3
Σ aromatics	10.9	18.0	15.0	10.8	33.1	26.1	24.2	25.6	19.8
Oxygenates									
acetaldehyde	4.1	4.0	4.3	4.7	3.1	13.3	..	3.5	8.1
acetone	7.8	4.4	11.6	12.0	8.3	9.8	9.7	4.2	2.1
Σ oxygenates	11.9	8.4	15.8	16.7	11.4	23.1	9.7	7.8	10.7
Σ unknown gc peaks (N)	8.7(9)	10.7(9)	17.4(9)	14.6(8)	24.7(16)	16.9(12)	19.0(16)	12.9(10)	17.4(11)
acetylene	2.8	4.8	2.5	3.2	2.6	6.0	6.2	7.5	7.4
Total NMHC	87.4	104.0	93.6	102.1	114.4	171.3	143.3	108.5	106.2

Table 7. SUMMARY AND ANALYSIS OF SMOKY MOUNTAIN HYDROCARBON DATA

Time:	9-25-78 6:00 AM	9-25-78 10:00 AM	9-25-78 12:00 PM	9-25-78 2:15 PM	9-25-78 4:00 PM	9-26-78 8:25 AM	9-26-78 8:30 AM	9-26-78 10:00 AM	9-26-78 11:30 AM
ΣP	47.4	49.3	36.1	44.8	35.0	75.5	64.1	41.5	39.8
ΣO	5.6	12.8	6.7	12.0	7.6	23.7	18.8	13.3	11.2
ΣA	10.9	18.0	15.0	10.8	33.1	26.1	24.2	25.6	19.8
$\Sigma P/C_2H_2$	17.1	10.3	14.3	14.0	13.5	12.5	10.5	5.6	5.4
$\Sigma O/C_2H_2$	2.0	2.7	2.7	3.8	2.9	3.9	3.1	1.8	1.5
$\Sigma A/C_2H_2$	3.9	3.7	5.9	3.4	12.8	4.3	4.2	3.4	2.7
$\Sigma NMHC/C_2H_2$	31.6	21.7	37.0	31.9	44.2	28.5	23.4	14.5	14.3
% vehicular emissions	54	78	46	53	38	60	73	117	119
% biogenic emissions	3	5	5	6	6	4	2	5	1

p-xylene were unresolved in this series of samples (due to GC modifications) and therefore may be biased high. Nevertheless, even a 6% biogenic contribution to the observed low concentrations of TNMHC is small, considering the sampling proximity to one of the most diverse, densely vegetated areas in the United States. An important contributing factor to the Smoky Mountains lush vegetation is the high rainfall that often exceeds 90 inches per year; this amount is second only to the Pacific Northwest in the United States. Thus the argument furthered by Sandberg et al. (21) that a direct correlation should exist between an active growing season and high biogenic hydrocarbon concentrations is not supported in the Smokies. That the low vegetative density of the San Francisco Bay area could produce hydrocarbon levels greater than the Smokies seems therefore unlikely.

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16. ABSTRACT

A critical review of the literature reveals nonmethane hydrocarbons in rural and remote areas consist mainly of anthropogenic species, and are composed of less than 10% biogenically-related compounds (i.e., monoterpenes and isoprene). Despite these results, some investigators continue to invoke "natural hydrocarbon emissions" to explain naturally occurring haze, incorrectly identified gas chromatographic peaks, and high concentrations of total nonmethane hydrocarbons that are measured by indiscriminate (total hydrocarbon-methane) analyzers. In response to the suggestion that biogenic emissions are responsible for the high hydrocarbon concentrations described in several reports, the Environmental Sciences Research Laboratory of the U.S. Environmental Protection Agency initiated short-term sampling as a means of validation. A limited number of whole-air samples were collected in Tedlar bags and analyzed by gas chromatography with flame ionization detection. The areas of study included: Tulsa, Oklahoma; Rio Blanco County, Colorado; and the Great Smoky Mountains in Tennessee. Tulsa air was found to contain an average of 0.2% isoprene of the total nonmethane hydrocarbon load. Rio Blanco County and the Smoky Mountain air, respectively, averaged about 2% and 4% biogenic hydrocarbon of the total non-methane hydrocarbon loads. Isoprene appears to be a dominant olefin in rural and remote areas.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
* Air pollution * Hydrocarbons * Biological productivity * Chemical analysis Gas chromatography	Tulsa, OK Great Smoky Mountains Rio Blanco Co., Colorado	13B 07C 08A 07D

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